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Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically?

I. Oref and B. S. Rabinovitch

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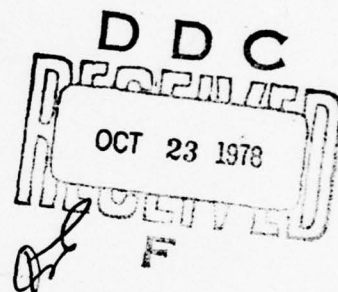
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Existing literature is surveyed and critically analysed. A variety of excitation techniques including crossed molecular beam, laser, photochemical, chemical activation and thermal are considered. Models of collisional perturbation relaxation and energy transfer are compared with literature evidence. The answer to the title question is yes.		

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DO HIGHLY EXCITED REACTIVE POLYATOMIC MOLECULES BEHAVE ERGODICALLY?

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Introduction

The past several years have seen considerable controversy on the subject of intramolecular vibrational relaxation. We consider only complex, polyatomic species at high levels of internal excitation characteristic of unimolecular reaction. Most molecules have thresholds above 30-40 kcal mole⁻¹. The contemplation of their relaxation behavior has brought together the interests of chemists and physicists.

The question is this: Do reacting molecules display ergodic or nonergodic behavior? That is, does an ensemble of reacting molecules explore uniformly all regions of its available internal energy-coordinate hypervolume (statistical behavior) prior to decomposition. Or is only a portion of phase space visited during the lifetimes of the molecules (non-statistical behavior)? Considerable effort has been devoted to the clarification of this question. The dilemma was phrased during the 1950's as follows: Which is more correct — the theory of R. A. Marcus and O. K. Rice or that of N. B. Slater?¹ Marcus and Rice (RRKM) employed a statistical model which postulated that coupling of the internal motions led to rapid intramolecular energy randomization on a time scale short relative to the lifetime of decomposing species (ergodic behavior). Slater characterized a molecule by a potential function having only quadratic terms and internal normal modes of motion which are orthogonal to each other, so that the system does not relax throughout its vibrational manifold (non-ergodic behavior).

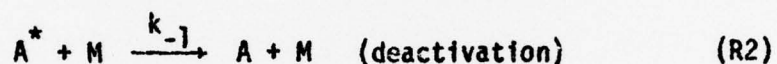
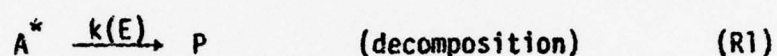
Indeed, this problem was resolved in favor of statistical models for molecules having lifetimes longer than $\sim 10^{-10}$ sec.² Evidence obtained in the 50's and 60's supported the ergodic proposition. Notwithstanding, the contrary view has been advanced.^{3,4} In recent years, various calculational and experimental studies including trajectory calculations, crossed beam experiments and laser excitation work have questioned anew the validity of statistical models. The ergodic question also appears in collisional phenomena. Intermolecular vibrational energy transfer between highly excited polyatomic molecules and bath molecules involves some type

of accommodation in a short-lived complex.⁵ The extent of intramolecular relaxation within the loosely bound compound species is a related problem.

We first sketch some background related to unimolecular rate formulations. Then we take up some types of experimentation that lead to useful conclusions with regard to the question at hand. The treatment represents particular viewpoints rather than a comprehensive review.⁶

Models for Unimolecular Decomposition.

An activated species A^* at the internal energy level E undergoes two processes:



R1 is decomposition with rate coefficient $k(E)$; R2 is collisional deactivation by a bath molecule, M ; the rate coefficient k_{-1} can be calculated with varying degrees of sophistication. In the simplest case (strong collision), A^* is deactivated below the threshold energy for decomposition, E_0 , by a single collision. If more than one collision is needed to deactivate A^* , then M is a weak collider with relative efficiency $\beta < 1$. Deactivation can encompass all aspects of intermolecular energy transfer $V \rightarrow V$, $V \rightarrow R$, $V \rightarrow T$, where V indicates vibrational, T translational and R rotational energy. The subject has been reviewed recently.^{5,7}

Slater's model¹ for $k(E)$ postulates nonergodic behavior in which decomposition occurs when a critical coordinate q extends beyond a critical length q_c . The molecule does not sample the whole of phase space and q is obtained by a superposition of various normal coordinates closely associated with the breaking bond. The RRKM transition state model^{1,8-10} applies in simplest form to reactions having a large potential barrier in both directions; internal energy is statistically distributed among the vibrational modes of the molecule and of the activated complex. Then,

$$k(E) = \Sigma P(E^+)/h F N(E) ; \quad (1)$$

$N(E)$ is the density of states of the excited molecule; $\Sigma P(E^+)$ is the number of accessible internal states of the complex; $E^+ = E - E_0$; h is Planck's constant;

F is a correction for centrifugal energy effects. $N(E^*)$ can usually be calculated quite accurately;^{9,10} $\Sigma P(E^*)$ is harder to evaluate since the frequencies of the complex are not known; however, certain procedures (fitting the Arrhenius A factor) ensure that reasonable values are assigned. A molecule for which $k(E)$ can be evaluated by the above procedure is called an RRKM molecule. There are conjectural, as well as known cases, however, where $k(E)$ may not fit the experimental magnitude.^{3,11-16} This could arise because of a "bottleneck" in phase space or because of a time scale for reaction which prevents statistical redistribution of the internal energy prior to decomposition. Such behavior is called, respectively, "intrinsic" and "apparent" non-RRKM behavior.¹⁶

Techniques of Excitation.

There are basically two ways to produce the excited species A^* . One is in a thermal Boltzmann system^{9,10} in which the molecules of the ensemble are transported above the threshold E_0 by collisions.^{9,10,16-27} The second way is by some "external" energy source or mechanism not subject to the equilibrium distribution law of canonical ensembles. Such sources include chemical activation,^{11-13,28-42} multiphoton excitation,⁴³⁻⁷² molecular beams,⁷³⁻⁹² single photon excitation,⁹³⁻¹⁰⁶ and photosensitized reaction.¹⁰⁷⁻¹¹² The hot molecules produced are subject to collisional intervention unless collision-free conditions are maintained.

The overall unimolecular rate coefficient is¹⁰

$$k = \int_{E_0}^{\infty} \frac{I f(E) k(E)}{k(E) + k_{-1}(M)} dE \quad (2)$$

where $E = E' + E_{th}$; E' is the effective energy introduced into the molecule by the excitation process; E_{th} is the original thermal energy of the molecule; $f(E)$ is the energy distribution function, such as the light source profile in the case of photochemical reaction; I is the flux of the excitation source.

For an equilibrium system, $E' = 0$, $E = E_{th}$, $f(E) = B(E_{th})$, $I = Bk_{-1}(M)$ and

$$B(E)dE = \frac{N(E) e^{-E/RT} dE}{\int_0^{\infty} N(E) e^{-E/RT} dE} \quad (3)$$

For a weak collider bath there is depletion of the substrate populations below E_0 ; $B(E)$ is replaced by its steady state value $B_{ss}(E)$ which can be found by an iteration method⁹ or by eigenvalue solution of the steady state matrix. According to eq. 2, the decomposition behavior of the excited molecule is independent of the origin of the excitation.

Thermal Systems.

This method is the oldest that has been applied. Resolution of the question of ergodicity of molecules prepared for reaction by random collisions is not necessarily one of simple test. Both the Slater and the statistical Rice-Ramsperger-Kassel (RRK) theory lead to classical expressions for the rate coefficient that are similar in form:

$$k_S = \frac{k_\infty}{\Gamma[(n+1)/2]} \int_0^\infty \frac{x^{(n-1)/2} \exp(-x) dx}{1+x^{(n-1)/2} \theta^{-1} \omega^{-1}} \quad (4)$$

and

$$k_{RRK} = \frac{k_\infty}{\Gamma(s)} \int_0^\infty \frac{x^{s-1} \exp(-x) dx}{1 + [x/(x+b)]^{s-1} A \omega^{-1}}$$

where θ is a quantity related to molecular parameters; A is a constant; ω is the specific collision rate; $b = E_0/RT$; $x = E/RT$; and n and s designate relevant internal degrees of freedom. Distinction between the two formulations could be difficult: sufficient flexibility may be provided by the choice of n and θ , in the first expression, or of s in the second, so as to bring about near-coincidence in the predicted magnitudes of k and of the falloff behavior (the decline of k with decreasing pressure).

However, certain choices of substrates make a distinction unequivocal.² Consider the isomerization of cyclopropane to propylene. Cyclopropane has D_{3h} symmetry and 7 of the 21 normal vibrational modes are degenerate. The Slater treatment predicts¹ that the maximum number of modes that contribute to the reaction coordinate is $n \leq 21 - 7 \leq 14$; the experimentally observed number is^{1,2} $n \approx 13$, in good agreement. However, if the symmetry of cyclopropane is reduced by substitution,

as in 1,2-cyclopropane- d_2 , then the allowed maximum value of n rises to $n \approx 17-18$. However, no such increase was found,^{17b} in accord with statistical theory.

Similarly, for the isomerization of methyl isocyanide to acetonitrile, a molecule with C_{3v} symmetry in which 4 of the 12 modes are degenerate, the observed value of $n \approx 4$ does not change¹⁸ as the progressive substitutions are made: $CH_3NC(C_{3v}) \rightarrow CH_2DNC(C_1) \rightarrow CD_3NC(C_{3v})$. Indeed, for a number of molecules, e.g., cyclobutane decomposition¹⁹ and cis-trans olefin isomerization,²⁰ symmetry restrictions cause failure of the Slater theory predictions for the falloff behavior. Good agreement exists with the predictions of statistical theory. These systems illustrate a way for distinguishing ergodic and nonergodic behavior even for a collisionally prepared ensemble of reacting molecules. Remarks that apply to Slater's extreme "normal-mode" form of theory also extend, more or less, to other variants^{4,101-103} of orthogonal modes theory.

It has been suggested⁴ that the random distribution may not only be prepared by collision but may also be maintained by (elastic) collisional perturbations with cross sections a 100-fold larger than conventional kinetic values. This could take place on a time scale short with respect to reaction so that intramolecular energy randomization is simulated even for intrinsically non-RRKM molecules. This is one of several arguments that have been offered in the past few years as an alternative to the generality of the central assumption of statistical theory; it will be considered in the next section.

Recent trajectory calculations on methyl isocyanide (with an assumed molecular potential) have led Bunker and co-workers^{3,16} to conclude that it is an "intrinsic" non-RRKM molecule with an internal bottleneck to redistribution of energy. The segmentation of the phase space of a molecule into two parts (Fig. 1) leads to the prediction¹⁶ of a false, premature high pressure limit (represented by point c) followed by a subsequent rise of a "part molecule" to the conventional limit at higher pressures (Fig. 2). The data on methyl isocyanide²¹ was considered to correspond to the false limit and early high pressure work by Harris^{3,22} indicated the occurrence of the predicted "part molecule" (Fig. 2) rise. (Of course, the bottleneck would not be evident and such rise could not occur in the collisional

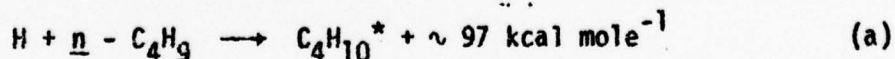
perturbation model.) More recent work²³ at pressures to 350 atm has revealed errors in the earlier report^{3,22} and confirms the high pressure limit of Schneider and Rabinovitch.²¹ Actually, RRKM theory gives good agreement with both the position and shape of the falloff for CH_3NC and for a series of isocyanides (CH_2DNC , CD_3NC , $\text{C}_2\text{H}_5\text{NC}$, $\text{C}_2\text{D}_5\text{NC}$). It is evident that a "part-molecule" bottleneck model is necessarily based on "happenstance" features of molecular potential (anharmonicities and couplings). It cannot explain the behavior for CH_3NC or the rest of the series.

Several other thermal unimolecular systems have been examined experimentally up to supra-high pressures to test for any alteration in k_∞ . Ethyl cyclobutane up to ~ 200 atm. showed a small decrease in rate which is attributed to a volume of activation, i.e., a many-body effect.²⁵ Nitryl chloride²⁶ showed no deviation from RRKM behavior up to ~ 300 atm. At ~ 300 atm, nitrogen pentoxide²⁶ showed a small change in k_∞ which the present writers believe represents only experimental complications.

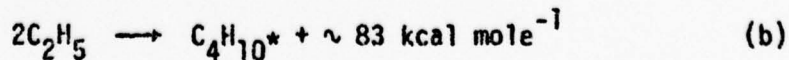
In conclusion, RRKM behavior in thermal systems has been tested to very high pressures. The results indicate overwhelmingly that no verified deviations from RRKM behavior have been seen. The theory continues as a working model and, when suitably modified, applies also to reactions involving low reverse barriers.²⁷

Chemical Activation Systems.

Chemical activation involves production of internally excited species by chemical reactions.²⁸ Association reactions are the most unequivocal with respect to the energy level of the product, e.g.,



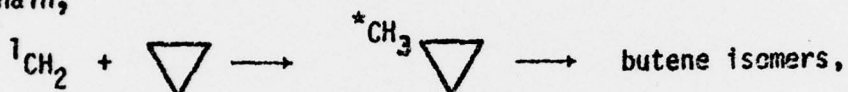
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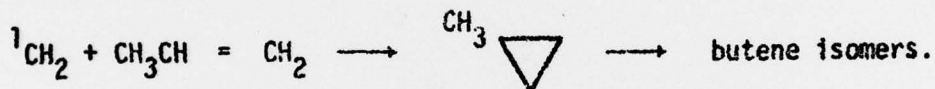
Different activation reactions can excite a molecule in different ways, i.e., a molecule may be injected into different regions of the space that describes its internal state (Fig. 1). Thus, reaction (a) deposits a high proportion of the

excitation energy in C-H stretching motions of the nascent butane. In reaction (b), the initial excitation heavily involves C-C stretching and skeletal motion. For non-ergodic behavior of excited butane, C-H and C-C rupture would be facilitated in (a) and (b), respectively.

Early chemical activation experiments showed that rapid intramolecular relaxation occurs after the excitation event; that the initial subset of highly excited vibrational modes of motion of the nascent molecule relaxes rapidly into the full set of internal motions. Thus, the proportions of the olefin products from methyl cyclopropane are independent of the activating reaction,²⁹ whether centered on the side chain,



or centered on the ring,



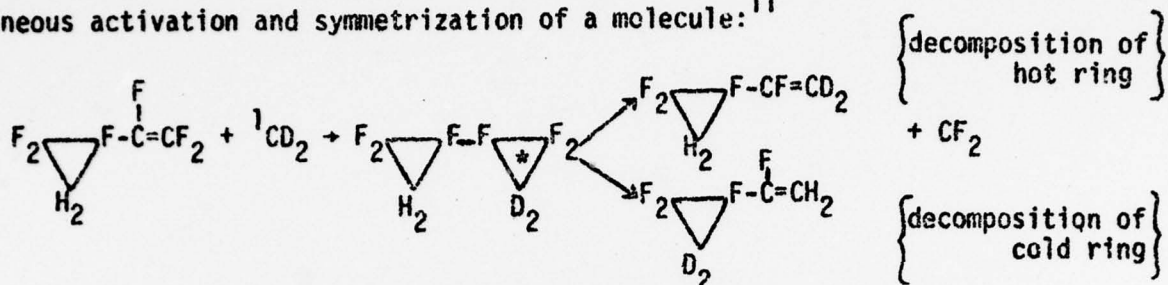
Many such examples have ramified over the years.

A variety of chemical activation experiments have revealed good adherence between statistical theory and the microscopic specific rates, $k(E)$. Examples are the series of 2-alkyl radicals³¹ from C_4 to C_{16} , at pressures up to 200 atm,¹⁴ with rate constants from 10^7 to 10^3 sec^{-1} ; a series of alkyl cyclopropanes,³² and the analogous perfluoroalkyl members, having specific rates over the range 10^{10} to 10^5 sec^{-1} ; and a truly multitudinous and impressive series of haloalkane molecules C_2 , C_3 and C_4 , studied by Setser and co-workers,³³ whose rates change from $\sim 10^5$ to $\sim 10^{11} \text{ sec}^{-1}$.

Possibly not all large polyatomic molecules obey statistical theory although reliable exceptions are difficult to find.³⁴ The vinyl^{35a} and the ethyl^{35b} radical decompositions are so mentioned, although further work is necessary and complete theoretical treatment requires careful consideration of conservation of angular momentum.³⁶

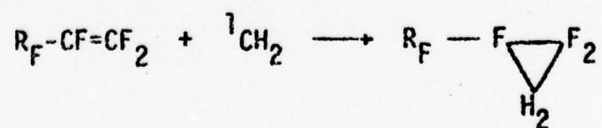
The studies described above say nothing about the time scale of the intramolecular relaxation. It must be substantially faster than the decomposition

process since RRKM behavior is manifested. In recent years experiments have been designed to measure the relaxation constant. The first study involved the simultaneous activation and symmetrization of a molecule:¹¹



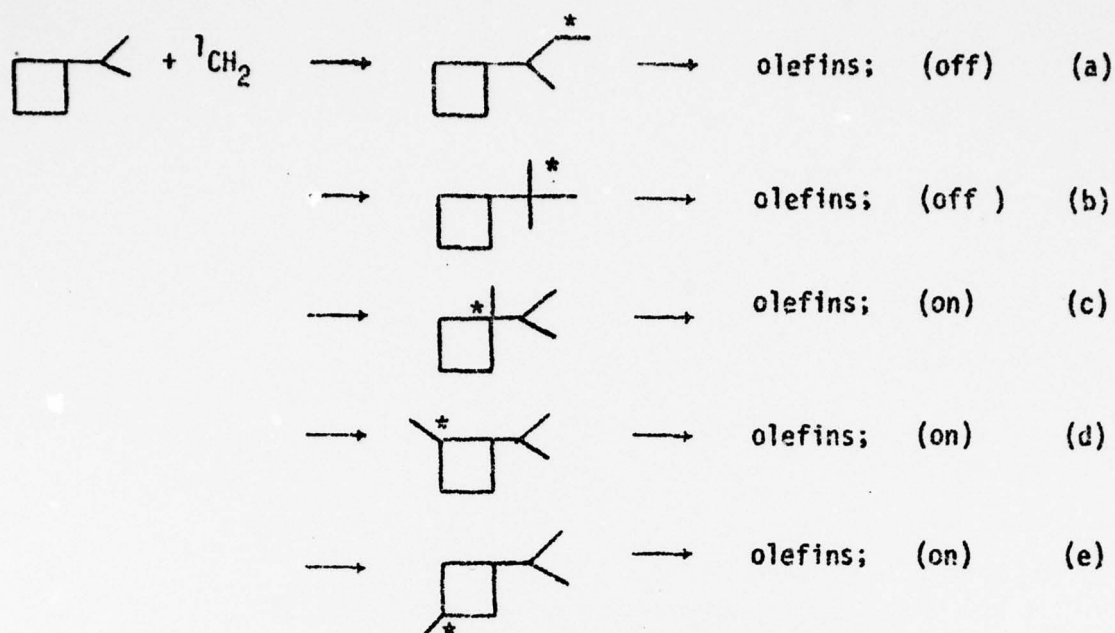
The H and D substituents simply label the hot (*) "nascent," and cold "old" rings. Excitation corresponds to injection of the molecule into its phase space (point b, Fig. 1) in a position proximate to the critical plane for rupture of the nascent ring (line y, Fig. 1). Internal energy randomization (diffusion of the system into the body of the phase space) competes with decomposition of the non-randomized molecule (diffusion across the plane, y). Decomposition of the nascent ring predominates at high pressure since molecules can diffuse only in small numbers through the phase space (internal randomization) to the critical hyperplane for rupture of the old ring before being deactivated by collision. Theoretical analyses of the proportions of non-random decomposition of the nascent ring, stabilization, and decomposition of randomized molecules leads to the value for the intramolecular relaxation constant, $\lambda \approx 10^{12} \text{ sec}^{-1}$.

Decomposition of the members of a homologous series was also studied,¹²



where $R_F \equiv \text{CF}_3$, C_3F_7 and C_5F_{11} . Again the values $\lambda = 1(\pm 0.4) \times 10^{12} \text{ sec}^{-1}$ were found.

More recently, alkyl cyclobutanes¹³ hydrocarbons were investigated. This provides a gross selection of the initial non-random state of excitation of the activated molecules, as illustrated for isopropyl cyclobutane substrate:^{13b}



"off" indicates initial excitation off, and "on" indicates excitation on the ring. The reaction in each case is ring rupture to form olefins whose structures are diagnostic of the particular source (a) to (e). Reaction (a) represents excitation at a site farthest from the ring, corresponding to injection of the "methyl" isopropyl cyclobutane molecules into regions of phase space remote from the critical plane for decomposition (point a in Fig. 1). The excited species cannot decompose until energy randomization occurs, i.e., the subset of initially excited vibrational motions must expand to include ring motions. By reaction (c), excitation takes place on the ring, i.e., the molecule is injected into a part of the phase space proximate to the dividing reaction plane (point b in Fig. 1). The initial subset of excited vibrations includes ring motions and the non-randomized molecule may decompose in competition with internal relaxation. The study of methyl cyclobutane substrate^{13a} led to the estimate, $\lambda > 5 \times 10^{12} \text{ sec}^{-1}$. The isopropyl cyclobutane system^{13b} provides values of $\lambda \approx 2.9 (\pm 0.5) \times 10^{12} \text{ sec}^{-1}$. Latest work on neopentyl cyclobutane system^{13c} also gives $\lambda \approx 2.1 (\pm 0.5) \times 10^{12} \text{ sec}^{-1}$. Within the uncertainty of the experiments, these values are several-fold larger than those for fluorocarbons.

Work in progress on the bicyclobutyl substrate^{13d} reveals similar behavior.

It has been suggested³⁷ that unlike photoactivation, chemical activation cannot illustrate non-random effects. The rationale for this proposal is that the reaction event, unlike light absorption, causes a perturbation of the nascent molecule that effectively couples the whole molecule. (By contrast, some proponents of the view that internal relaxation in reacting systems is not invariably fast cite chemical activation such as the vinyl and ethyl radical systems, mentioned earlier,³⁵ as examples of their model.) This proposal is designed to support the proposition that RRKM theory only appears to give a quantitative account of data, but in the view of the writers it falls of its own weight. If a nascent molecule is profoundly perturbed, such also must be the case by the principle of microscopic reversibility for a highly extended or decomposing molecule, no matter what its original mode of excitation, and randomness should apply. Moreover, the cyclopropane and cyclobutane systems just described demonstrate that energy randomization does not occur upon formation of the hot species by chemical reaction but is a process that follows excitation with a characteristic smallest relaxation constant of $\approx 10^{12} \text{ sec}^{-1}$. In any case, it is not a sufficient condition for obedience to RRKM behavior that an ensemble of molecules is formed initially with microscopic energy distributions that follow random statistics. Indeed, this postulate was used in the classical Slater theory. It is also requisite that a statistical redistribution of energy be maintained on a time scale that is short compared to the chemical degradative process so that the energy above E_0 is available in the reaction coordinate. The redistribution can be obtained via the intramolecular mechanism or by the intermolecular collisional perturbation process proposed by S. A. Rice and co-workers.⁴ However, the collisional perturbation mechanism is itself contrary to a variety of experimental evidence:

First, chemical activation studies of the butyl radical were shown some time ago⁴⁰ to be independent of pressure down to pressures below 10^{-2} torr, i.e., at nominal collision rates $\sim 10^5 \text{ sec}^{-1}$ (relative to decomposition rate constants

$\geq 10^7 \text{ sec}^{-1}$) where collisional redistribution would be inadequate. A number of such low-pressure cases are known.

Second, in the intramolecular relaxation studies cited in refs. 11 and 36, the effects of internal relaxation become observable at pressures of 0.2 - 20 torr where the nominal collision rate is only $10^6 - 10^8 \text{ sec}^{-1}$ (elastic values $\sim 10^8 - 10^{10} \text{ sec}^{-1}$). By contrast, the internal relaxation occurs on a scale of 10^{-12} sec , i.e., much less than collision intervals.

Third, crossed molecular-laser beam experiments (explicitly designed to be collision free) on a wide variety of complex molecules such as SF_6 , SF_3Cl , etc. (see later) have been shown by Lee and co-workers⁴¹ to be in accord with various aspects of statistical RRKM theory.

Finally, the ultraviolet excited decomposition of internally converted cycloheptatrienes under very low pressure collision-free conditions has been shown recently to accord well with statistical theory.⁴²

Single and Multi-photon Vibrational Excitation.

Laser-induced unimolecular decomposition is of great current interest.⁴³⁻⁷² (Extensive references are cited in these papers; the mechanism of multiphoton absorption^{54,57,58} need not be discussed here.) Multiphoton infrared laser excitation brings about activation of a molecule by irradiation at a particular frequency. The average energy of a photon from a CO_2 TEA laser source is $\sim 3 \text{ kcal mole}^{-1}$ and the number absorbed is above 30 in some cases. The cardinal question has been — do molecules decompose in a mode-specific manner or do they explore the potential surface prior to decomposition?

There is mounting evidence that multiphoton induced decomposition of molecules exhibits ergodic behavior.^{41,47,48,60-62,66b} However, the term "collisionless region", frequently used, usually refers to conventional kinetic cross sections. A test of the elastic collisional perturbation model requires pressures that are a hundred-fold smaller. Many experiments in the "kinetic" collisionless region were not at low enough pressure to provide a clear test.

The clearest support from laser studies of the statistical approach is given by the work of Lee and co-workers.^{41,46-48} Several crossed molecular beam - CO₂ laser experiments on the dissociation of SF₆, halomethanes, etc., give spatial distributions of products and lifetime estimates in accord with RRKM theory. Other laser work does not provide as unequivocal a test. In some cases, at least part of the data are in the "kinetic" multi-collision pressure region, i.e., $k_{-1}M > k(\epsilon)$ (eq. 2). In other cases, the specific rate constants are not known or not given, and it is impossible to say whether $k_{-1}M < k(\epsilon)$, a necessary condition for "elastic" collisionless behavior. Nevertheless, important information is provided by this work. They correspond very well to the predictions of the statistical model; they show little evidence⁵⁶ for mode-specific decomposition. Setser and co-workers⁶² irradiated CH₂FCH₂Br at the C-F stretching frequency under kinetic collisionless conditions. This should favor HF elimination if non-ergodic behavior occurred. The product ratio was HBr:HF = 10:1 as predicted by statistical theory since HBr is eliminated with lower threshold energy than HF. In another study,⁴⁵ CCl₂F₂ was excited in the multicollision region, first at the CCl₂ stretching frequency and then via the CF₂ stretching mode. The reaction products were identical in both cases. Dissociation of ethylacetate⁶¹ under conditions of low pressures and high laser intensity gave rate coefficient consistent with RRKM theory. "Collision-free" dissociation of CF₂Cl₂ and CF₂Br₂ produces⁶⁰ vibrationally excited CF₂ in which the energy is distributed statistically and can be characterized by a vibrational temperature T_v . The decomposition of CH₂F₂⁶⁹ follows the thermodynamically predicted route of fission of the C-H bond.

Laser isotope separation in large polyatomic molecules has been the subject of a large number of investigations.^{54,71,72} No novel theories need yet be invoked for the interpretation of the decomposition process.

Some confusion with regard to internal relaxation has arisen in laser studies due to use of inappropriate models for intermolecular energy transfer at the high

energies concerned.^{70a} Collisional activation/deactivation by cold bath molecules is principally V-T,R (i.e., the internal modes of the cold bath molecule do not relax) and takes place on every collision.^{5,70a} However, the efficiency of V-T,R transfer may decline dramatically at higher bath temperatures⁵ and the correct models to be used in partially, or completely collisionally equilibrated, high fluence laser systems are not well known. There can be V-V transfer between highly excited molecules in the neat gas^{63,64} in systems where the absorbed energy per molecule is high.^{45,50,62} This process is different from vibrational energy transfer at low levels of excitation⁶⁵ as shown in energy mapping on methyl halides.⁶⁶⁻⁶⁸

The above systems involve multi-photon excitation. With higher energy photons, only one^{59a} or a few photons^{59b} are absorbed prior to decomposition. The decomposition of formic acid has been studied as a function of pressure using an HF laser.^{59b} Only three photons of $10 \text{ kcal mole}^{-1}$ cause decomposition. The authors propose that intramolecular energy relaxation takes place following the photoexcitation.

An interesting experiment is single photon ($\sim 7300 \text{ \AA}$) isomerization,^{59a} $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{NC}$. Good agreement was obtained with RRKM calculations, although the authors invoked a more elaborate mechanism to explain the results. The molecule was assumed to be non-ergodic with intramolecular energy redistribution assisted by collisions. This mechanism has been criticized in an earlier section. So far, molecular ergodicity provides a simple, consistent explanation of this experiment.

Molecular Beam Systems.

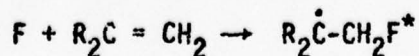
A chemically activated reaction in crossed molecular beams takes place under truly collision-free conditions. Many ingenious experiments have been executed. Information is obtained on the spatial and velocity distributions of the products. A "long-lived" ($\gtrsim 10^{-12}$ sec) collision complex undergoes many rotations prior to decomposition and gives a symmetric product distribution relative to the center-of-mass vector. This is the case for some reactions of an atom with an alkali halide molecule,⁷³ Cs , $\text{K} + \text{RbCl}$ and⁷⁴ $\text{Ca} + \text{NaCl}$, which form a three-center complex;

for bimolecular reactions of CsCl with KCl and KI, which form a four-center complex;⁷⁵ and for atom + polyatomic molecule, Cs + SF₆;⁷⁶ K, Rb, and Cs with SnCl₄ and SF₆;⁷⁷ Cl + olefin⁷⁸ and F + olefin.^{13,79} Thus, many nominally bimolecular reactions are examples of fast unimolecular processes.

The question is whether the available internal vibrational-rotational energy of a long-lived complex is randomized. Interpretation of the data is subject to physical, and sometimes computational constraints. One model which has been used to explain product translational energy distribution is derived from RRKM theory.⁸⁰ A potential which takes into consideration the long range (r^{-6}) interactions and centrifugal energy of the complex is employed. The translational energy in the reaction coordinate, plus the potential energy of the centrifugal barrier are assumed to convert to translational energy of the products. The calculated translational energy distribution was found to agree with the experimental distribution in the reactions CsCl + KCl, KI;⁷⁵ Cs + SnCl₄, SF₆⁷⁶ and K, Cs + RbCl.⁷⁴

Vibrational energy transfer involves the extent of intramolecular relaxation in a collision complex. In many cases, the behavior is non-ergodic and the internal degrees of freedom of the cold bath molecule do not relax.⁵ The models of refs. 5 and 80 have been used to interpret the results of inelastic scattering of vibrationally excited KBr by polar molecules.⁸¹ In these cases V-T and, for very polar bath gas (CH₃NO₂), V-V transfer are observed and large amounts of energy are removed (10-30 kcal mole⁻¹). The interpretation of the results has been questioned⁸² since conservation of probability was not observed. An expression which provides obedience to the conservation rules and detailed balance has been given in ref. 7.

A system which has been studied very carefully under velocity selected conditions is the decomposition^{13,79} of C₂H₄F* and alkyl substituted fluoroethyl. The excited radicals were activated by the reaction



The angular distribution of the decomposition products indicates that the radical has a lifetime which is much longer than the period of rotation. The average

lifetimes of excited fluoroethyl radicals measured in chemical activation systems⁸⁵ accord well with RRKM theory. A major finding of Y. T. Lee and co-workers was that the translational energy distribution of the products seemed to be at variance with statistical theory. As the reactant energy increases, the fraction of the product energy that appears as translation remains constant; it was expected that the fraction would go down since the excess energy should be distributed among the internal modes. Assumption of only a limited number of effective vibrational degrees of freedom to explain the translational distributions results in unreasonably short lifetimes.

RRKM theory makes no statement about the disposal of reverse barrier potential energy. Its relative distribution between translation and internal modes depends on the shape of the surface. Dynamical constraints are not considered in the calculation of the rate coefficient for the decomposition of the excited molecule. For cases where system angular momentum is of the same order of magnitude as molecular angular momentum, calculation of exit channel translational energy can prove extremely complicated.^{7,83} Recently, Worley and Marcus⁸⁶ developed a statistical adiabatic extension of RRKM. A distinction between loose and tight complexes is made. For a loose complex in the exit channel, no coupling of radial and internal coordinates exists and the final product distribution reflects the internal distribution of the complex. This is a restatement of the model of ref. 80 discussed above. In the case of a tight complex, coupling between radial and internal coordinates affects the final product energy distribution. Bending vibrations in the complex become free rotations of the product. Because of the wider spacing of the vibrational compared with the rotational levels, the adiabatic transformation of the former into the latter causes a shift to higher product translational energies. This occurs when coupling between various modes of the complex and the products is introduced. This model was applied to $(\text{CH}_3)_2\dot{\text{C}}\text{-CH}_2\text{F}^*$ and reasonable agreement was obtained between experimental and calculated⁸⁶ energy distributions. There is better agreement between experiment and statistical theory than with loose⁸⁷

transition state theory.

In a series of experiments which complement beam work, McDonald and co-workers⁸⁸ studied the internal energy of products by the arrested relaxation of infrared chemiluminescence. The vibrational emission of product molecules was measured. Fluorine and chlorine substitution reactions $F + C_2H_3Y$, $F + C_6H_5Y$, $Cl + C_2H_3Br$, $Cl + C_6H_5Br$, and $Cl + C_3H_5Br$, where Y is H , CH_3 , Cl or Br , were investigated. Nonrandom distribution of vibrational energy was observed for product molecules with density of internal states less than 10^4 states/cm⁻¹. Of course, statistical behavior is expected only when the density of states is high. In a trajectory study⁸⁹ on the internal energy distribution following chemical activation of methane-d₃ and chloromethane-d₃, it was shown that the energy becomes randomized in less than 5×10^{-12} sec.

Charged particles reactions are not discussed here for lack of space. The important work of Wolfgang⁹⁰ and Henglein⁹¹ on ion-molecule crossed beams showed that intramolecular energy redistribution in the collision complex occurred on the time scale of 10^{-12} sec. Statistical theory has been applied in mass spectrometry under the name of Quasiequilibrium Theory (QET).⁹² It is found that for polyatomic ions with lifetimes from 10^{-3} sec to 10^{-11} sec randomization of energy takes place prior to decomposition. Where exit channel interactions exist, it is necessary to modify statistical QET to obtain agreement between calculated and experimental translational energy distributions. Cases involving isolated electronic states are excluded.

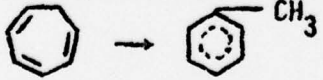
Photochemistry. Vibronic Excitation

There are common features of internal energy disposal between photochemical reactions and gas phase emission spectroscopy. The molecules can be in an excited electronic state, such as S_1 or T_0 , or in the ground state S_0 following internal conversion. Multichannel decomposition from various excited levels can occur. Only a few selected topics are considered here.

The reactant molecule produced in photo-excitation may be identified with A^*

of reactions R1 and R2 presented earlier. The rate constant is calculable via an expression similar to eq. 2. The assumption is made that internal energy is statistically distributed among all the modes of the electronically excited molecule.^{15,93-95} The value of $k(E)$ can be calculated from eq. 1 provided that the vibration frequencies of the excited molecule and activated complex are known, not a very certain situation in many cases.

There are cases where it cannot be assumed a priori that energy will be statistically distributed among all internal modes. Consider the photodecomposition of azoalkane,¹⁵ $R-N=N-R \rightarrow 2 R + N_2$. Excitation is via the $n \rightarrow \pi^*$ transition on the nitrogens. The decomposing bonds are R-N adjacent to the initially excited bond. Intramolecular energy relaxation of the energy into all the available modes appears fast, with rate coefficient^{11-15,81-84} $> 10^{11} \text{ sec}^{-1}$. If the system can be intercepted after a short time (high pressures), it is possible to obtain decomposition exclusively from an initially excited moiety in which most of the excitation energy resides. The expected behavior is a curved Stern-Volmer plot and such curvature has been observed.¹⁵ Now $k(E)$ for randomized $C_2H_5N=NC_2H_5$ is expected, and found to be larger than that for $C_3H_7N=NC_3H_7$, which in turn is larger than that for $C_4H_9N=NC_4H_9$. By contrast, the value of $k(E)$ for decomposition from the (identical) excited nascent moiety in each molecule is not expected to change much and was found to be relatively constant.

Internal conversion of S_1 to S_0 produces a vibrationally hot molecule. If internally relaxed, the value of E_0 should be identical to that for thermal decomposition of the same species. Indeed, for the collision-free isomerization of cycloheptatriene to toluene,^{42,97} , E_0 was found to be the same for the thermal and photoisomerization processes.

Radiationless (reactive and radiative) processes and products ratios are, naturally, a function of the level of excitation. Provided that the vibrational manifold is dense enough and the level of excitation high enough, ergodicity is observed⁹⁹ in the decomposing molecules; otherwise, single vibronic level chemistry may be observed.¹⁰⁰⁻¹⁰⁵

Photosensitization.

Photosensitization is a useful method for exciting an acceptor via electronic energy transfer from a donor molecule.¹⁰⁶⁻¹⁰⁹ Unlike sensitization in condensed media where low vibrational states prevail, gas phase processes can take place from an excited internal state in the higher electronic manifold.

A model has been proposed,^{15,110} which assumes statistical partitioning of excess internal energy E_T between donor and acceptor. The following is an example. The Cd(5^3P_1)-sensitized decomposition of C_2H_3F is found¹¹² to have a higher quantum yield than the benzene (3B_1)-sensitized decomposition. Both have almost the same triplet energy. The reason for the higher yield of the Cd- C_2H_3F pair, according to the model, is that the donor has no internal modes and can carry away only translational energy. Benzene has many internal modes so that the acceptor acquires less of the available energy; $k(E)$ is smaller and the quantum yield is reduced.

The partition of E_T between donor and acceptor molecules is also exemplified by the singlet transfer in benzene-aniline gas mixtures.¹¹¹ The quenching of benzene fluorescence by aniline was investigated. It was found that the available internal energy is distributed between acceptor and donor in a statistical manner.

Photophysics

Photophysical experiments are another source of information. The available models vary from those that postulate that the excited molecule is ergodic prior to electronic relaxation^{99,100} to those that predict local mode behavior wherein bond excitation is uncoupled from the other molecular modes.¹⁰¹⁻¹⁰³ The rules that govern photophysical processes are similar to those for reacting systems: at low levels of excitation, i.e., low density of states, the radiative decay process has the specific traits of the excited mode^{100,104} and it is possible to follow the behavior of a single vibronic level;¹⁰⁵ for large polyatomic molecules at high levels of excitation, the internal energy relaxes through the vibrational manifold of the excited electronic state.¹⁰⁰ Examples of single level behavior at low levels of excitation are benzene¹⁰⁴ and cyclobutanone;¹⁰⁵ as the level of benzene

excitation energy increased, the fluorescence quantum yield dropped due to intramolecular energy transfer. CHCCl , CHCBr ¹⁰¹ and H_2CO ¹⁰⁵ are examples of small molecules where similar behavior was observed. In large molecules like tetracene and pentacene^{100a} at high levels of excitation, it was found that intramolecular energy redistribution occurs on a time scale shorter than electronic energy relaxation; but naphthalene has been reported to be a contradictory case.^{100b} The above findings cohere generally with the results of McDonald^{88,89} and agree with the major features of reactive systems.

The Dependence of the Intramolecular Relaxation Constant on E

We may speculate on the dependence of the observed (smallest) intramolecular relaxation constant λ on the energy content of the molecule. A pragmatic hybrid curve for large fluoromolecules such as SF_6 and $\text{CF}_3\text{-C-C}_3\text{F}_4\text{D}_2$ may be constructed. In an elegant experiment, Deutsch and Brueck¹⁰⁶ excited the ν_3 mode of SF_6 with a CO_2 laser to the $\nu=3$ level ($\sim 9 \text{ kcal mole}^{-1}$). They showed that ν_3 comes into equilibrium with other degrees of freedom with a time constant of $\sim 3\mu \text{ sec}$ i.e. $\lambda \approx 3 \times 10^5 \text{ sec}^{-1}$. Obviously, $\lambda \rightarrow 0$ for relaxation of the $\nu=1$ level, for which small vibration theory works well, so that a curve of λ vs E is asymptotically horizontal at low energies. For fluorocyclopropanes, at a total energy of $\sim 115 \text{ kcal mole}^{-1}$, it has been shown above^{11,12} that $\lambda \sim 10^{12} \text{ sec}^{-1}$. Since classical dynamical considerations restrict increase in λ beyond $\sim 10^{13} \text{ sec}^{-1}$, the curve of λ vs E is asymptotically vertical at higher energies. Figure 3 represents the combined behavior. The area between the curves, A, is an arbitrary representation of the region of uncertainty and cannot be probed for these molecules by kinetic studies since they decompose at energies above $45 \text{ kcal mole}^{-1}$ ($E_0 \approx 45 \text{ kcal}$, $\text{CF}_3\text{-C-C}_3\text{D}_2\text{F}_4$; $E_0 \approx 86 \text{ kcal}$, SF_6). The study of related molecules, such as N_2F_4 , for which E_0 is only $19 \text{ kcal mole}^{-1}$ might be counterproductive for the reason described later. How general such curves are, especially for hydrocarbon,^{100b} remains to be seen.

The region A is a potentially fruitful subject for theoretical delineation. Various treatments of the temporal and amplitude evolution of a set of anharmonic oscillators^{4,113} have been given. In general, some degree of stochastic behavior seems assured if the anharmonicity and coupling of the members of the set is

sufficiently great and if the total energy of the set is sufficiently large. The often postulated "bottleneck" to internal relaxation of energy is a consequence of the occurrence of non-overlapping resonances which "traps" the energy of the set for a number of vibrational cycles of the motion. The overlap of resonances can lead to stochastic behavior.^{113h} Several recent treatments^{113f-h} suggest that overlapping behavior may result if the energy in a particular mode is greater than 0.7-0.9 of the bond dissociation energy D , or if the total energy E exceeds some critical criterion value E_c , which depends on the potential function and may be less than or greater than D . However, the degree of stochastic behavior required to rigorously satisfy statistical theory may be much greater than that which satisfies pragmatic experimental tests.^{113h} This difference can explain why it is that conventional statistical theories have such broad practical applicability.

In conclusion, it seems that the answer to the title question is "yes", so far, for reactive systems on a time scale $> 10^{-12}$ sec. The high hope of earlier laser experimentation — that mode-specific excitation could be carried out or would reveal non-statistical behavior — has failed to reveal any substantiated example. Most unimolecular studies have been made at moderate to high levels of excitation (40-100 kcal mole⁻¹); the possibility exists that such behavior could be detected at lower energies. Several molecules, such as N_2O_4 , dioxetanes, and N_2F_4 have reaction thresholds E_0 close to 15-20 kcal and suggest themselves as possible candidates. However, this may prove to be a vain hope because even though E_0 decreases, the existence of severe anharmonicities attendant upon bond rupture and the occurrence of a shallow col(s) near the configuration of critical extension of the molecule could lead to a concomitant decrease in the critical criterion value E_c . Conventional experimentation of adequate refinement is needed. A study in progress on $t\text{-C}_4\text{H}_9\text{O}$ decomposition ($E_0 \sim 15$ kcal mole⁻¹) by Batt is a hopeful possibility.¹¹⁴

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Figure Captions

Figure 1: After ref. 16a (I) RRKM molecule: Injection into phase space far away from (a) and close to (b) critical bounding plane for decomposition, y . Injection into b can cause apparent non-RRKM behavior under appropriate experimental conditions.

(II) Non-RRKM molecule: Injection into c is the reason for "false" high pressure limit caused by the "bottleneck," x . Injection into d causes the "part" molecule behavior. All points at constant energy.

(III) Thermal activation of an RRKM molecule.

(IV) Non-Boltzmann activation (chemical, photoactivation) into part of phase space.

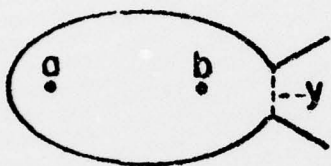
Figure 2: Unimolecular rate coefficient vs. pressure (after reference 16).
Fall off behavior for an "intrinsic" non-RRKM molecule having an internal bottleneck.

Figure 3. Internal energy vs. $\log \lambda$.

General behavior of intramolecular rate coefficient λ as a function of the internal energy. The area between the lines A is the region of uncertainty (see discussion). Points: 1) ref. 106; 2,3) ref. 14; 4) ref. 41; 5) ref. 11, 12

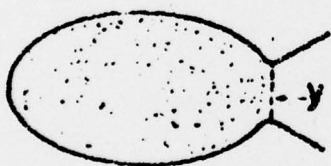
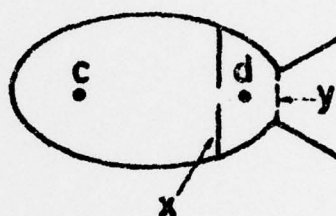
RRKM

I



Non-RRKM

II



III

Thermal
activation



IV

Non-Boltzmann
activation

Fig. 1

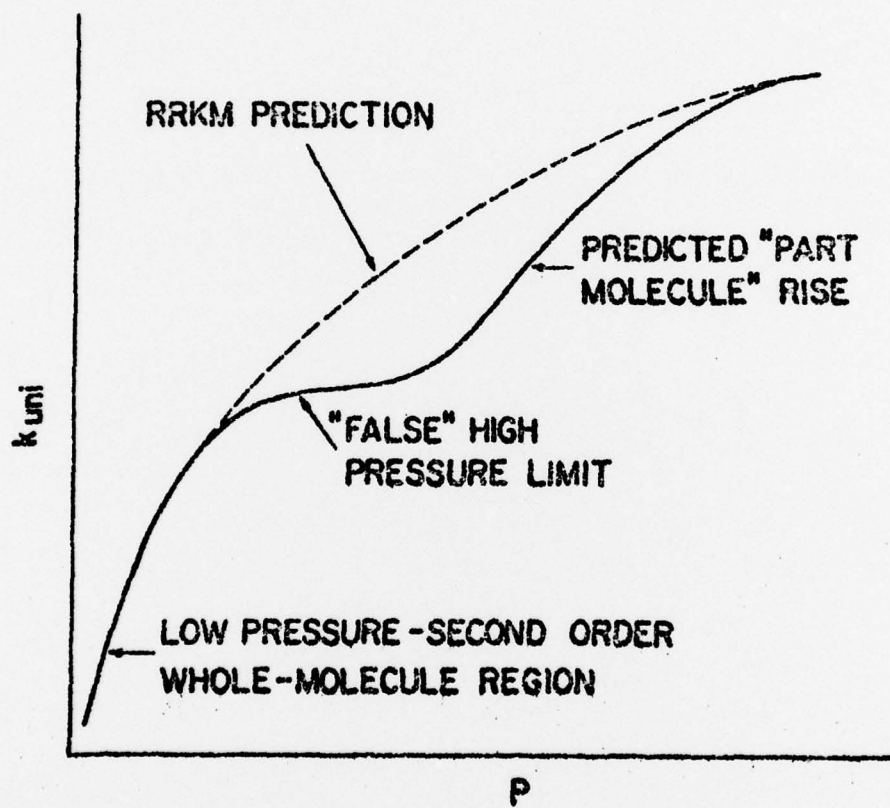


Fig. 2

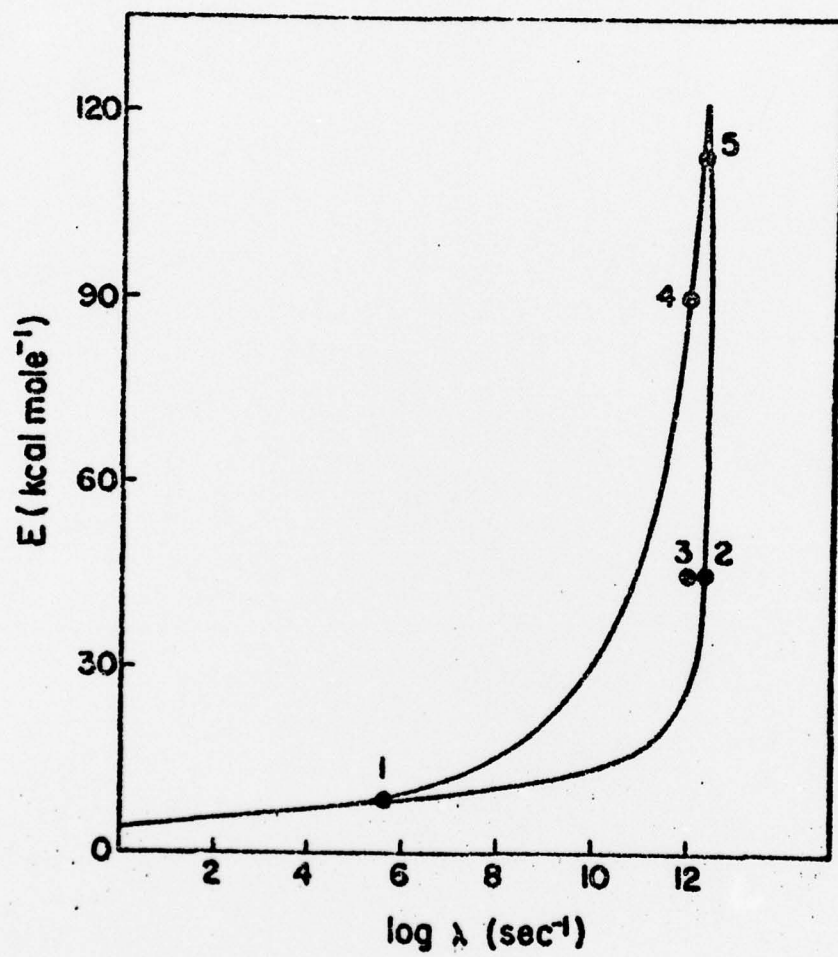


Fig. 3